LEBANESE UNIVERSITY

Université Libanaise

RESEARCH PLATFORM OF SCIENCES AND TECHNOLOGY

LEBANESE UNIVERSITY
FACULTY OF SCIENCES

Catalytic abatement of volatile organic compounds

Pr Madona LABAKI

Lebanese University

ULCO – Dunkerque

23rd june 2017

OUTLINE

- Volatile Organic Compounds (VOCs)

Definition, categories, legislations, source of emissions, impacts, treatment methods

- Catalytic oxidation
- Research needs

OUTLINE

- **Volatile Organic Compounds (VOCs)**

Definition, categories, legislations, source of emissions, impacts, treatment methods

- Catalytic oxidation
- Research needs

Volatile Organic Compounds (VOCs)

Definition

* Definitions of VOC vary depending on the country and legislation in question.
* Definitions based on vapour pressure, boiling points, and reactivity of organic species.

* According to European Solvent Emission Directive's:
"**any organic compound having at 293.15 K a vapour pressure of 0.01 kPa or more, or having a corresponding volatility under the particular conditions of use**."

* Most usual one in EU !

* Paint Directive:
''Volatile organic compound (VOC) means any organic compound having an initial boiling point less than or equal to 250 °C measured at a standard pressure of 101.3 kPa''.

Volatile Organic Compounds (VOCs)

Categories

* VOCs are numerous, varied, and ubiquitous.
* Many classifications

* They can be classified into different families defined by their chemical formulae, each of which possesses common properties, although there may be major differences in terms of toxicity

* A chemical classification
- Linear hydrocarbons, saturated or not
- Monocyclic and Polycyclic Aromatic Hydrocarbons (MAH) and (PAH)
- Oxygenated VOCs (OVOC) (aldehydes, alcohols, ketones,esters)
- Chlorinated VOCs (CVOC)
- Chlorofluorocarbons (CFC)
- Sulphur-containing VOCs (SVOCs)…

Volatile Organic Compounds (VOCs)

Categories

* VOCs are sometimes categorized by the ease they will be emitted

For example, the World Health Organization (WHO) categorizes indoor organic pollutants as:

Very volatile organic compounds (VVOCs)

Volatile organic compounds (VOCs)

Semi-volatile organic compounds (SVOCs)

Description	Abbreviation	Boiling Point Range (°C)	Example Compounds
Very volatile (gaseous) organic compounds	VVOC	<0 to 50-100	Propane, butane, methyl chloride
Volatile organic compounds	VOC	50-100 to 240-260	Formaldehyde, d-Limonene, toluene, acetone, ethanol (ethyl alcohol) 2-propanol (isopropyl alcohol), hexanal
Semi volatile organic compounds	SVOC	240-260 to 380-400	Pesticides (DDT, chlordane, plasticizers (phthalates), fire retardants (PCBs, PBB))

Volatile Organic Compounds (VOCs)

Legislations

* Many directives which differ from country to country

* **Last three decades**

* 1rst VOC addicted directive of the Council of the European Union (EU) in 1999

1999/13/EC (Solvent Directive):
"replace substances or preparations which, because of their content of VOCs classified as carcinogens, mutagens, or toxic to reproduction, are assigned or need to carry the risk phrases R45, R46, R49, R60, R61 … by less harmful substances or preparations within the shortest possible time".

1rst limit values for VOC emissions that were provided to be met by the year 2007

* Regulations become **more and more stringent**

Volatile Organic Compounds (VOCs)

Sources

Natural & **Anthropogenic**

Forests & Plants
Especially leaves
Terpenes are major

Stationary & Mobile sources

Industrial processes & gasoline distribution

Road traffic, marine transport, etc…

Outdoor

Indoor → Cooking, hair spray, furniture coatings, etc.

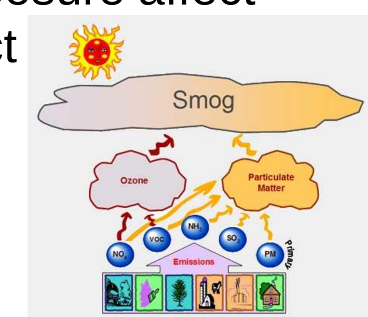
Volatile Organic Compounds (VOCs)

Impacts

Human health & **Environment**

* Dizziness, eye, nose and throat irritation, headaches, loss of coordination, nausea
* Damage to liver, kidney, and central nervous system
* Some of the VOCs are highly toxic, carcinogenic, or genotoxic

* The time and level of exposure affect the extent of a health effect



* Stratospheric O_3 depletion
* Higher ground level of O_3
* Greenhouse effect
* Tropospheric ozone increase
* Environmentally hazardous smog: HC + NOx + other airborne chemicals + sunlight $\Rightarrow O_3$
* Precursors of secondary pollutants
* Atmospheric oxidation of biogenic and anthropogenic VOCs = sources of carbonaceous aerosols

Volatile Organic Compounds (VOCs)

Treatment methods

Recovery

* Adsorption

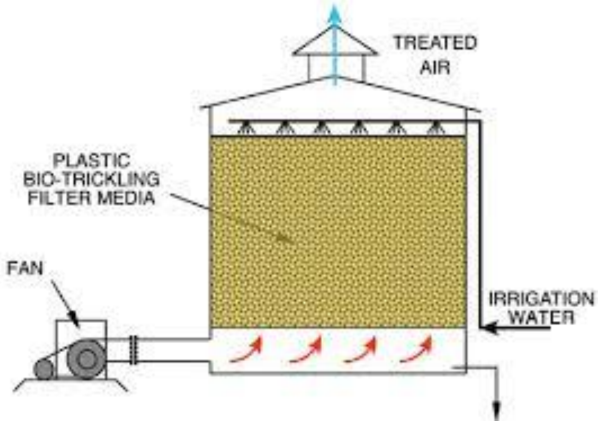
* Condensation

- Emission mixture not very complicated
- Economical value for the recovered chemicals: directly to the process or by selling

Destruction

* Biodegradation

* Incineration → Thermal / Catalytic



OUTLINE

- Volatile Organic Compounds (VOCs)

Definition, categories, legislations, source of emissions, impacts, treatment methods

- **Catalytic oxidation**
- Research needs

Catalytic oxidation

Advantages of catalytic incineration

The first examples of catalytic incinerators come in 1940s

* Suitable when the emission mixtures are complicated
* Applied from small total VOC concentrations to rather high concentrations
* Energy requirements < thermal incineration
* Abatement efficiency very high
* Thermal NOx formation minimized (temperature does not increase close to 1300 °C)

$$VOC + O_2 \rightarrow CO_2 + H_2O$$

Catalyst

Activity

Selectivity

Lifetime (stability)

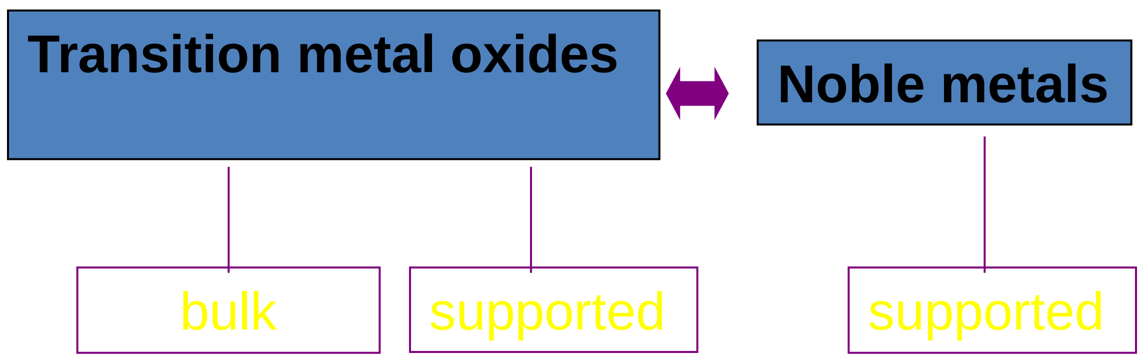
Cost

Catalytic oxidation

Catalysts

Catalyst = active phase ± support ± promoter

Active phase for VOC oxidation =



** The support*

better dispersion of the active phase

support-metal interaction

mechanical strength

thermal resistance…

Catalytic oxidation

Catalysts

Catalyst = active phase ± support ± promoter

Active phase for VOC oxidation = **Transition metal oxides** ⟺ **Noble metals**

- Transition metal oxides: bulk, supported
- Noble metals: supported

** Factors that affect catalyst performance*

preparation procedure

active phase, loading, and oxidation state

surface area of the catalyst and the dispersion of the active material

oxygen mobility and oxygen storage capacity (OSC) of a catalyst

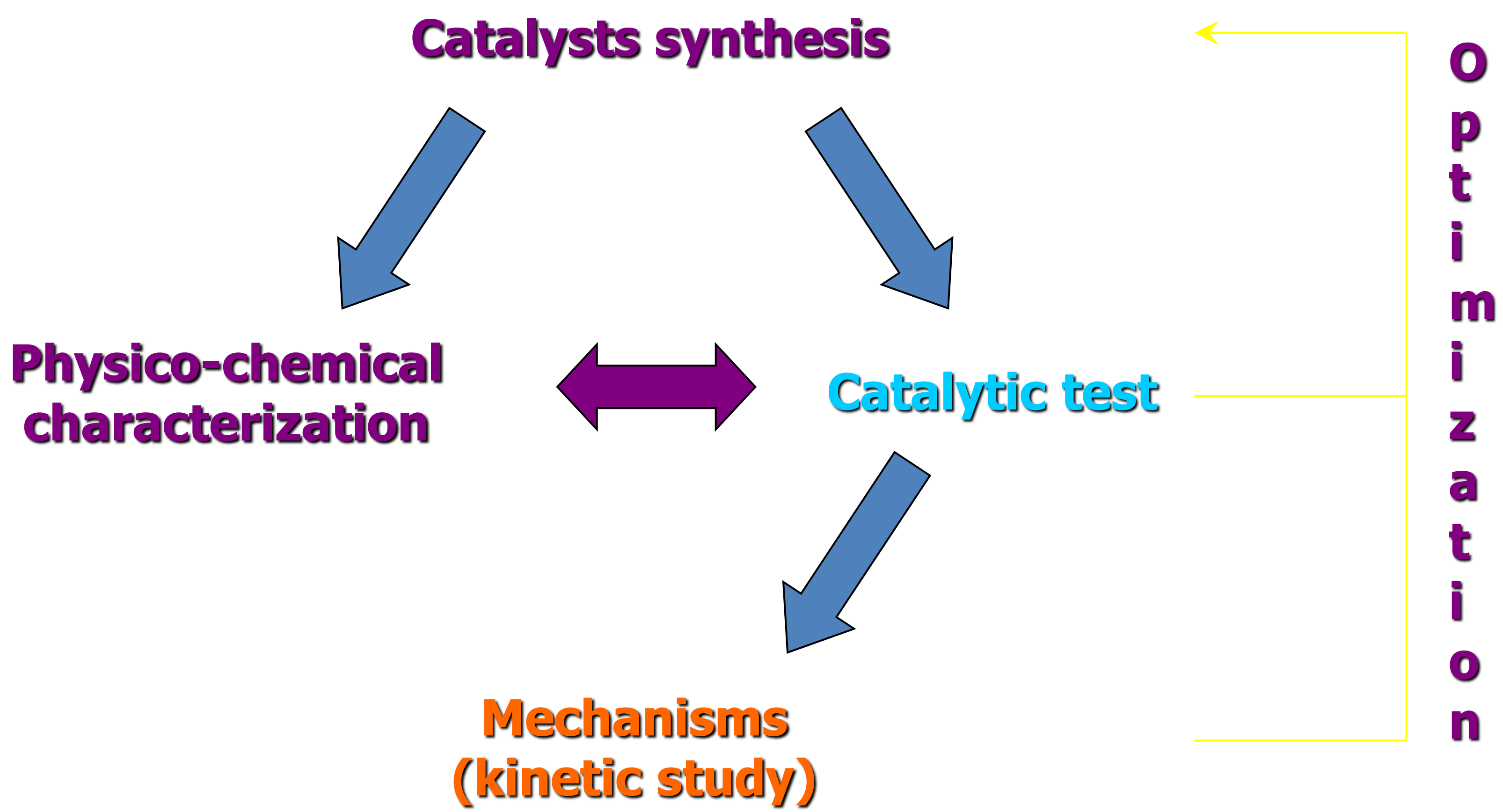
modifiers and promoters

precursor salts

process operation conditions such as temperature, pressure, and gas mixture composition

Catalytic oxidation

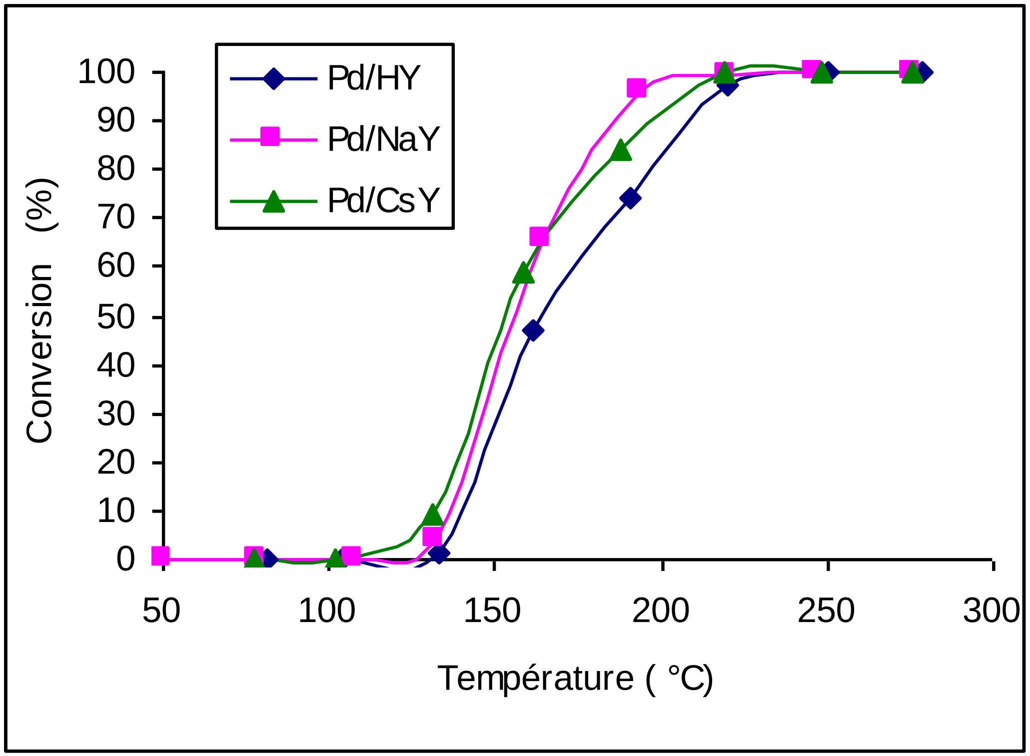
Catalysts



Catalytic oxidation

Examples

Noble metal Pd: support effect



Coke amount after test

Pd /CsY < Pd / NaY < Pd/HY

Higher acidity ⇨ higher amount of coke

M. Hosseini, L. Tidahy, S. Siffert, et al.

↳ **Influence of the electronegativity of the cation exhanged on the particle size of Pd**

Catalytic oxidation

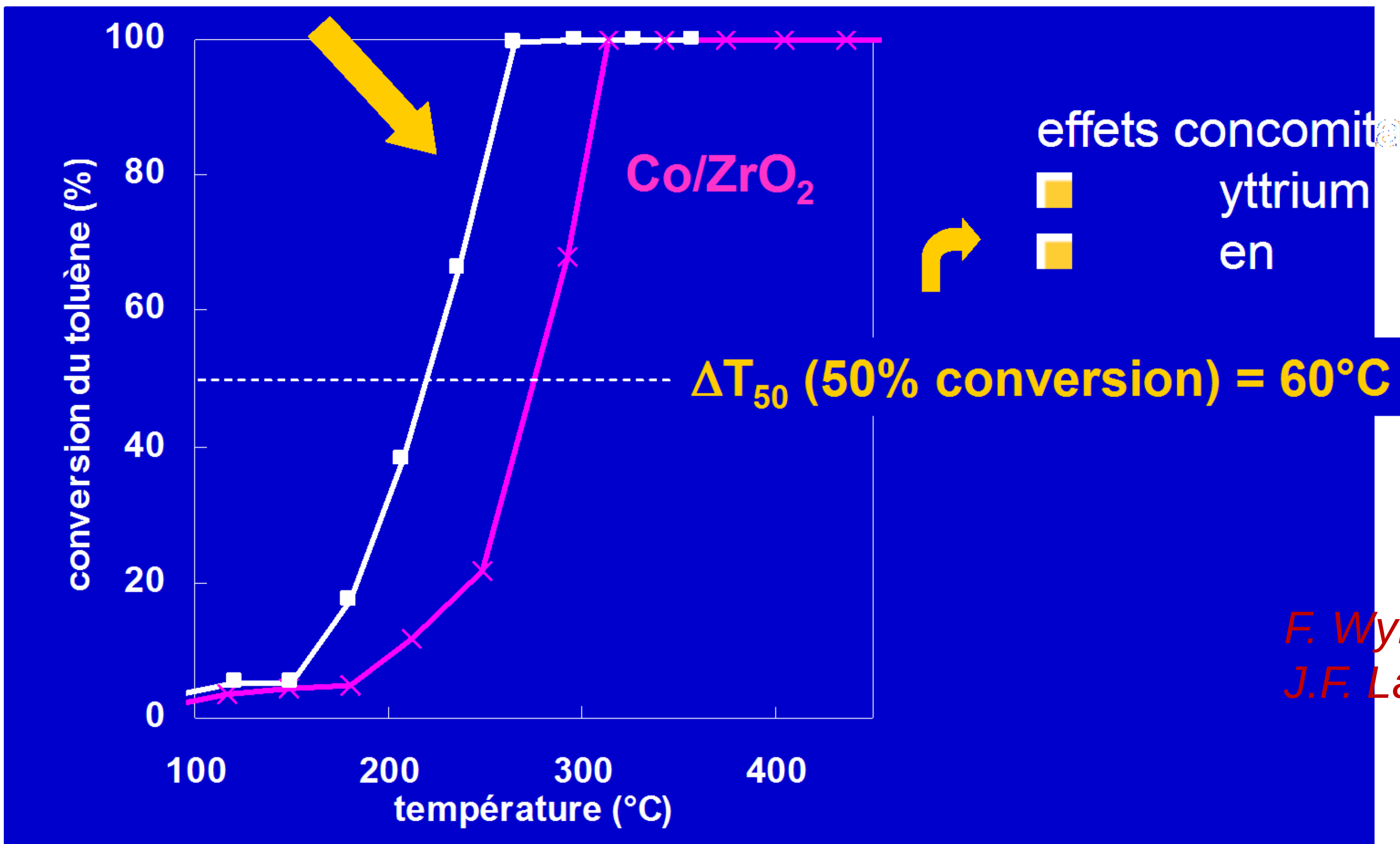
Examples

Transition metal cobalt, precursor & support influence

Cobalt supported on ZrO_2 (ZrO_2) and ZrO_2-(5%)Y_2O_3 (**Zr-5Y**)

Ethylene diamine (en) > nitrate

$Co(en)_1/Zr-5Y$

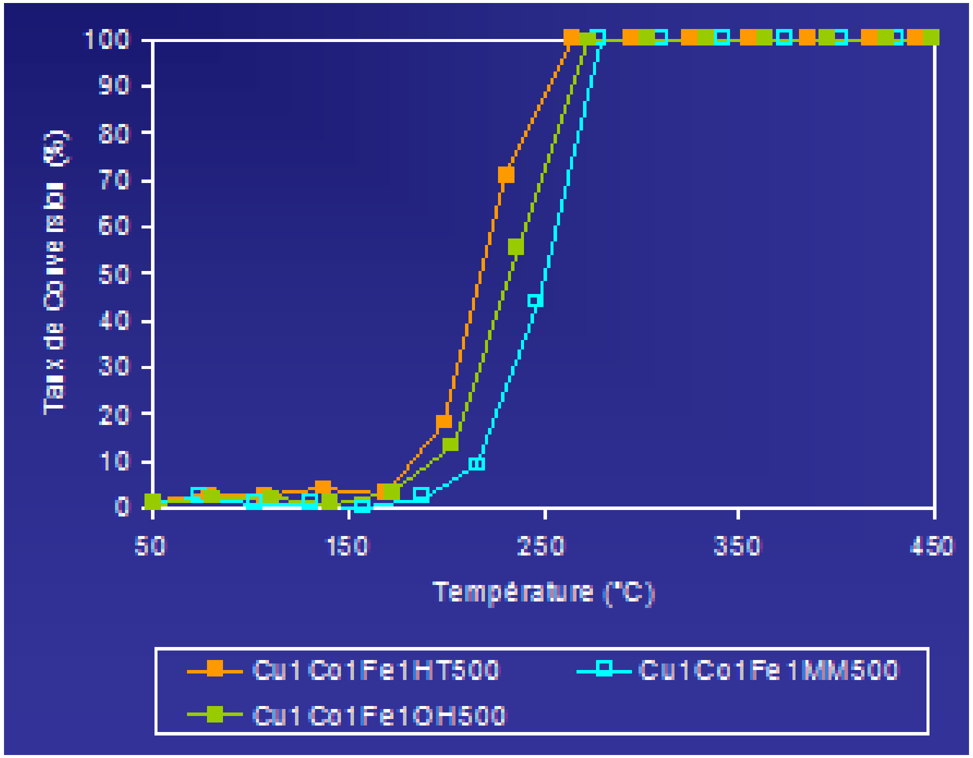


F. Wyrwalski, S. Siffert, J.F. Lamonier, et al.

Catalytic oxidation

Examples

Preparation method



Hydrotalcite > Hydroxide > Mechanical mixture

Phases Co_3O_4, $CoFe_2O_4$, $CuFe_2O_4$, $CuxCoyO_4$, CuO

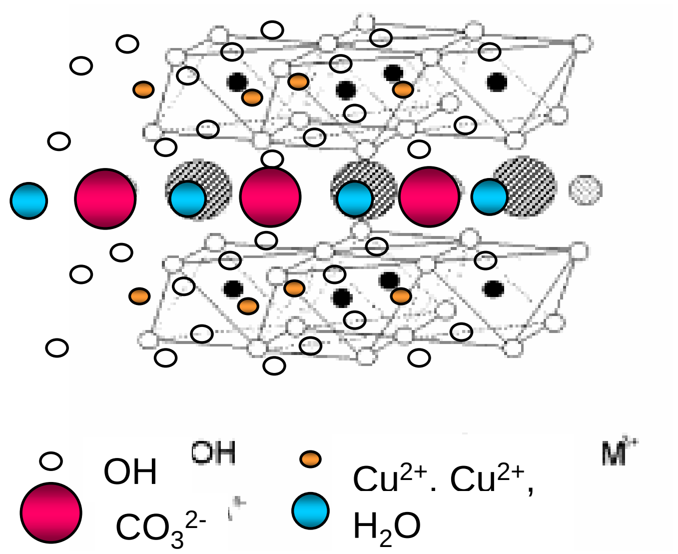
Preparation by hydrotalcite route gives high performances

C. Carpentier, S. Siffert, J.F. Lamonier, et al.

Catalytic oxidation

Examples

Hydrotalcite structure

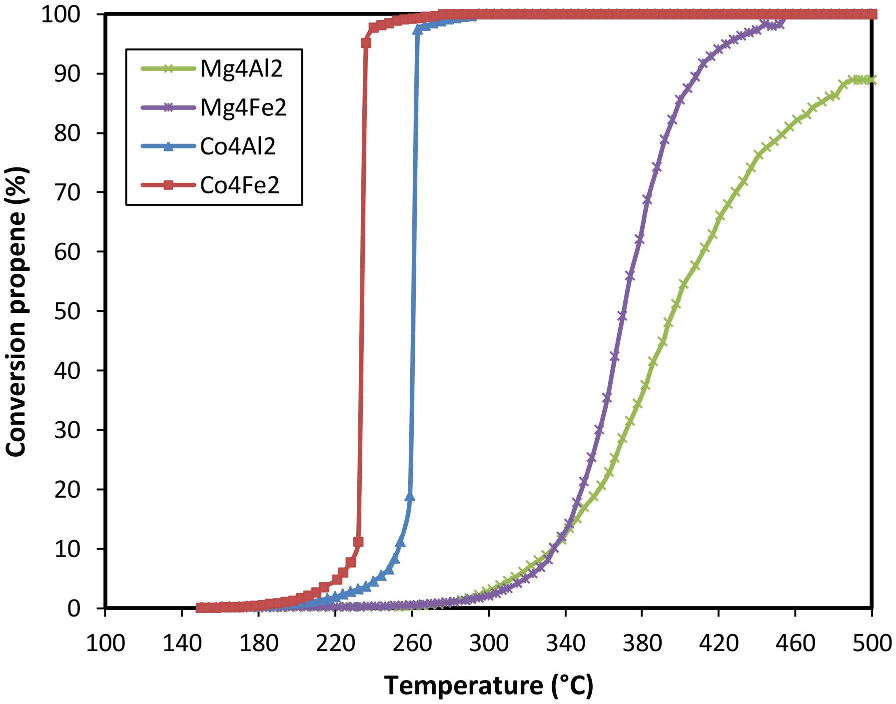


Good thermal stability, redox properties, acido-basic, high surface area, homogeneity

Catalytic oxidation

Examples

Nature of active phase



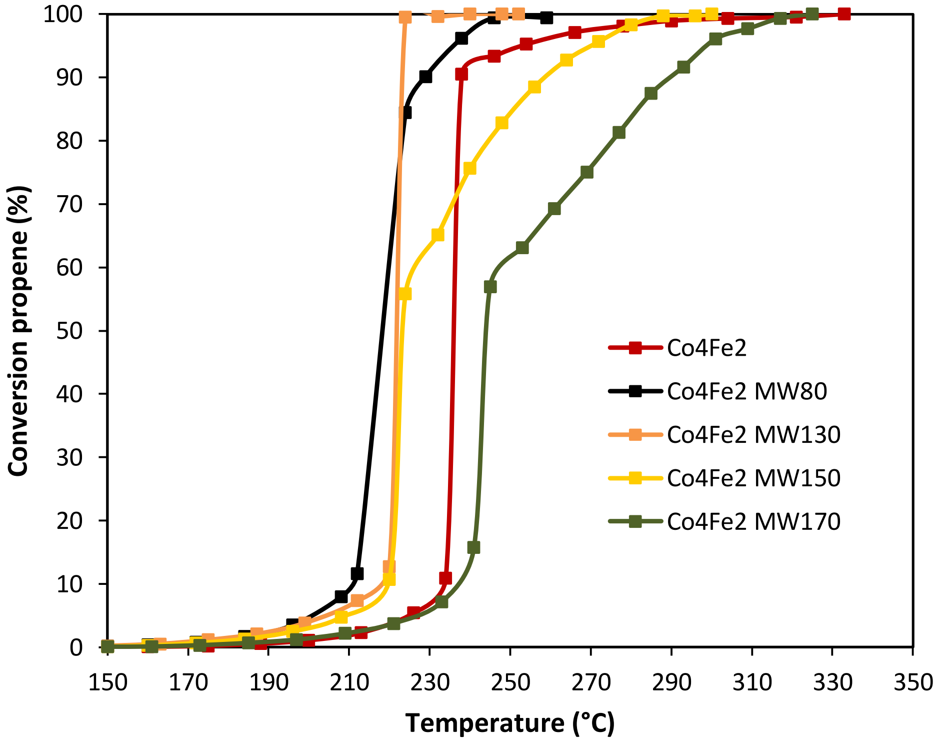
Propylene oxidation:
$Fe^{3+} > Al^{3+}$
$Co^{2+} > Mg^{2+}$

C. Abou Serhal S. Siffert, R. Cousin, et al.

Catalytic oxidation

Examples

Preparation method



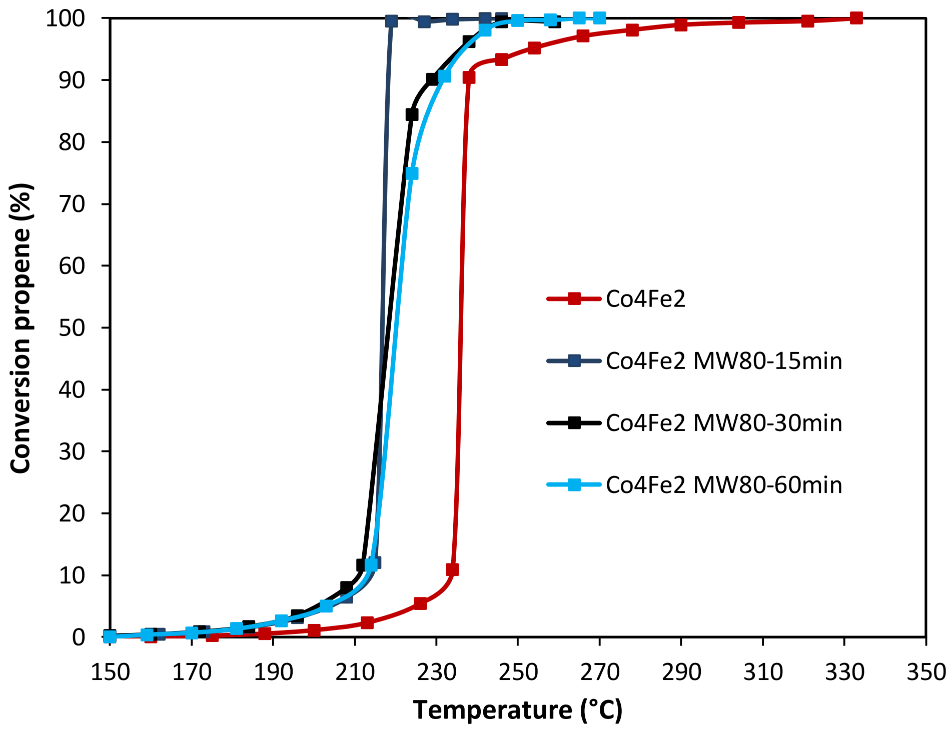
Propylene oxidation:
Influence of the temperature
during microwave irradiation

C. Abou Serhal S. Siffert, R. Cousin, et al.

Catalytic oxidation

Examples

Preparation method



Propylene oxidation:
Influence of time exposure to microwave irradiation

C. Abou Serhal S. Siffert, R. Cousin, et al.

Catalytic oxidation

Examples

Different VOC

* Decreasing order of reactivity over $LaMnO_3$ perovskites (Musalik-Piotrowska et al.):

Acetone = butyl acetates > ethyl acetate > toluene > n-hexane

* Competitivity towards adsorption sites

- Very difficult to predict the behavior of a VOC mixture
- In general, an inhibiting effect is rather predominant
  A promoting effect is rare

Examples:
On bulk perovskite: n-butyl acetate oxidation was strongly inhibited by n-hexane
On monolith perovskite: n-butyl acetate oxidation was strongly inhibited by n-hexane and toluene

Catalytic oxidation

Emerging technologies

Non-conventional catalytic oxidation

Different kinds of activation of the catalysts:

- **Light**

Photocatalysis: process that uses UV-light in the activation of the catalysts that are usually semiconductors such as metal oxides or sulfides

Useful for indoor air

Mainly TiO_2

- **Plasma**

Combination of non-thermal plasma and catalysis has also been tested in VOC oxidation

A catalyst improves the selectivity of non-thermal plasma process and the final conversions of the reactants

The plasma can affect catalyst properties, adsorption process, and thermal activation

- **Microwaves**

In some cases, a non-isothermal microwave-assisted (mw) catalytic process would be of Interest

Using of mw radiation in heating of chemical reactions has been of interest during recent years

OUTLINE

- Volatile Organic Compounds (VOCs)

Definition, categories, legislations, source of emissions, impacts, treatment methods

- Catalytic oxidation
- **Research needs**

Research needs

*** Scientific and market interest for environmental catalysis significantly expanded in the last 3 decades**

- continuously increasingly more stringent regulations on the quality of emissions and the environment

- increasing awareness of the central role that these catalysts play in the development of technologies to improve the quality of life and the environment

***** Catalytic oxidation of VOCs achieved considerable **success**

- **good activity: feasible at low temperature**
- **good selectivity: less amounts of toxic compounds**

***** VOC oxidation: in general, noble metal based catalysts more active than metal oxides but more expensive

Research needs

* **Challenges**

- Development of efficient catalytic systems that can oxidize a range of VOCs at much lower temperatures

- Catalyst deactivation is a major problem associated with catalytic oxidation. Catalysts can be easily deactivated by adsorption of water vapor and other intermediates

- Detection of intermediates and their further readsorption and oxidation

- Modelling of catalytic reactor performance should be developed for a pilot scale practic

- More research should be directed in the catalyst development effective under visible or solar light irradiation and also testing in indoor air pollution levels

- New applications ⇒ research to find new innovative solutions and technologies which will benefit all areas of catalysis as well other industries

Research needs

* **Challenges**

- Continuously tightening VOC emission regulations are bringing new challenges to the effectiveness of the current installations, but also new application areas for catalytic abatement.

- Due to this, new innovations are needed in designing of new more durable and selective catalysts and in the development of the current technology

- Changing towards hybrid systems

- Further reduction of the operating costs

- Making profit from the emissions by changing the wastes to valuable products

- Due to tightening regulations also the gas measurement systems should be developed further to for example ensure the efficiencies of the abatement units

Acknowledgements

- Lebanese University
- All the staff of the LCPM and PR2N
- University of Littoral – Côte d'Opale (ULCO)
- All the staff of the UCEIV and MREI
- University of Lille
- University of Haute – Alsace
- University of Balamand (UOB)
- Master 2 and PhD students
- Agence Universitaire de la Francophonie (AUF) – Région Moyen Orient
- Lebanese council for scientific research

Thank you for your attention